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Exhaust emissions of regulated and non-regulated pollutants of passenger cars

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Abstract: Exhaust emissions of VOC speciation, aldehydes and other carbonyl compounds, polyaromatics and regulated pollutants are measured using a vehicle bench on a sample of passenger cars. 30 diesel and gasoline cars are tested, complying with ECE 1504 to Euro 3 emission standards, according to 10 real-world driving cycles based on European driving behaviour, with some of them adapted to vehicle size. The emission results of this large-scale measurement campaign show the influence of vehicle technology and driving behaviour on the emission of 100 individual pollutants. In addition, the results are discussed per VOC group and compared with other studies. The influence of the successive emission standards on the emission factors is very positive in most of cases. However, whereas hot CO_2 is almost stable, diesel hot NOx, diesel hot and cold VOC, and the 6 most carcinogenic gasoline PAH have increased with standards. Diesel vehicles are less pollutant for CO, HC, CO_2, VOC, but more pollutant for NOx and PAH. The distribution of VOC species per molecular family highlights the fact that monoaromatics make up the biggest share (~88 and 62 % resp. for gasoline and diesel vehicles). The second family is the alkanes which contribute resp. 8 and 9% of the total mass of measured VOC. The majority of volatile PAH is observed in the gaseous phase, but the least volatile and the carcinogenic PAH are adsorbed more in particulate phase.

INTRODUCTION

The most recent state of the art in Europe on methods of estimating transport pollutant emissions [1-2] has shown that knowledge is of good quality regarding hot regulated emissions from light vehicles, up to the Euro 1 regulation. Regarding more recent vehicles (Euro 2 and 3, gas and common rail diesel vehicles), the database was obviously far less voluminous and more often than not only concerned regulated driving cycles bearing little resemblance to reality, whereas these vehicles make up a considerable share of traffic.

Regarding non-regulated pollutant emissions, several limited measurement campaigns have been carried out [3-9]. Most of these studies have been methodological, and when applied only dealt with a low number of vehicles using very recent technology and most often measured under conditions bearing little relation to reality.

The project, whose results are presented below, and in detail in [10], aims to extend our knowledge on the emission factors of the most recent passenger cars, particularly with respect to non-regulated pollutants, by applying cycles representing real European vehicle utilisation conditions. This research has been carried out in the framework of the European Artemis project, "Assessment and reliability of transport emission models and inventory systems" (www.trl.co.uk/artemis), aimed at developing the next European models for estimating transport emissions, of which the road model will replace Copert 3 in 2005.

1. METHOD

A sample of cars was tested in the laboratory with a large number of driving cycles, in order to measure regulated and non-regulated pollutant emissions and consumption.

Samples of vehicles

The vehicles tested were passenger cars mostly chosen from private owners with a distribution similar to that of the French fleet of 2001, although vehicles in conformity with the most recent standards were slightly over-represented. The gasoline and diesel vehicles conformed to emission standards ECE 1504 to Euro 3. Table 1 shows the distribution per fuel and standard of the sample as well as its mean characteristics.

sample		n	cubic capacity (cm^3)	power (kW)	weight (kg)	specific power (kW/t)	age (yrs)	mileage (Mm)
gasoline	Euro 1	3	1155	47.3	827	56.7	6.5	80
	Euro 2	6	1497	70.2	1096	63.3	2.8	31
	Euro 3	4	1477	70.5	1111	63.2	0.5	8
	total	*13*	*1412*	*65.0*	*1038*	*61.7*	*2.9*	*35*
diesel	ECE 1504	2	2201	57.0	1063	53.3	12.1	216
	Euro 1	3	1851	46.7	1028	45.5	6.0	128
	Euro 2	10	1931	67.3	1286	52.2	2.1	51
	Euro 3	2	1934	70.5	1275	55.3	0.5	14
	total	*17*	*1949*	*62.8*	*1213*	*51.5*	*3.7*	*80*

Table 1: Main characteristics of the sample of vehicles.

Within each category, vehicle models were chosen in order to represent the distribution of brands and models in the fleet as well as possible, while taking into account models made available by private owners (21 out of 30 cases).

Annual mileages of 13,500 km were observed for gasoline vehicles and 21,450 km for diesel vehicles, which is slightly higher than French mean values, respectively 12,180 and 20,030 km in 2004 [11]. The fuels used came from local service stations.

Driving cycles

The vehicles were tested on the INRETS' rolling test bench. This test bench has rated and maximum generating powers of respectively 93 kW and 132 kW, and rated and maximum torques of respectively 2114 Nm and 3000 Nm. It is equipped with a 1219 mm diameter roller. Vehicle inertia is simulated mechanically for 540 kg by systems in rotation and beyond this by the electric generator. Cooling of vehicles and especially engines was done by ventilation of ambient air as a function of vehicle speed up to 120 km/h, on a section of 0.8 m^2 situated in front of the radiator grille: thus cooling was comparable to that on the road.

The sample of vehicles was tested using a set of hot and cold driving cycles: 1 *Inrets court* cycle, 3 *Artemis* cycles, and 5 *VP faible/forte motorisation* cycles. Other cycles were monitored including standard cycles, though their results are not presented here. All the cycles monitored are ordered in Fig. 1 in terms of average speed and acceleration. It should be noticed that the accelerations are systematically higher than those of regulated cycles, at the same average speed.

Each set or family of cycles was formulated by statistical analysis on the basis of kinematics

recorded on European roads. A detailed description of the development and characteristics of these cycles can be found in different publications: [12-13] for *Inrets court* cycles, [14] for the European *Artemis* cycles, and [15] for the PV *faible/forte motorisation* cycles. The latter cycles are alternative and specific to vehicles with low and high powers respectively. This family includes two sub-families, one with 3 cycles and the other with 4 cycles, with the urban kinematics conditions represented respectively by 1 and 2 cycles (see Table 2).

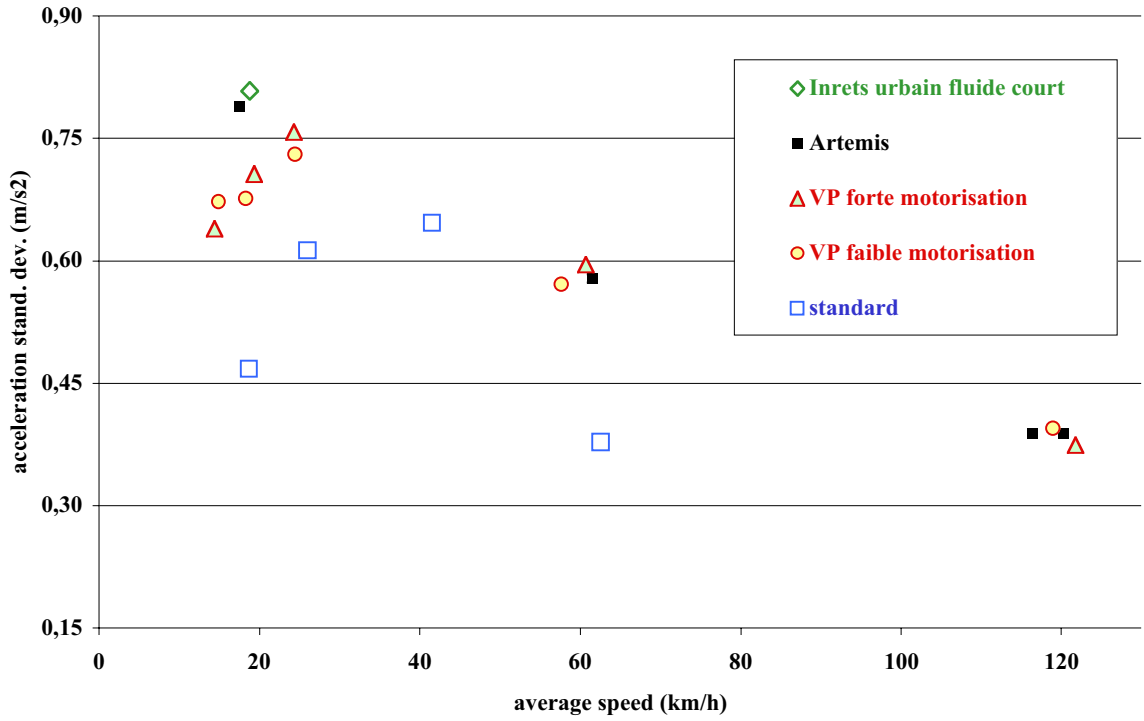

Figure 1: Description of cycles monitored in terms of average speed and standard deviation of acceleration, and standardised cycles for comparison.

cycle family	kinematic conditions					
	urban			rural	motorway	total
Artemis			*urbain*	*rural*	*autoroute*	
			29.2	44.9	25.9	100
VP faible motorisation	*urbain dense*	*urbain fluide*	*urbain*	*route*	*autoroute*	
	17.2	16.5	-	46.6	19.7	100
	-		33.7	46.6	19.7	100
VP forte motorisation	*urbain dense*	*urbain fluide*	*urbain*	*route*	*autoroute*	
	13.3	12.1	-	43.2	31.4	100
	-		25.4	43.2	31.4	100

Table 2: Names of cycles and their weights in the total vehicle mileages.

In addition, in table 2 we indicate the weight of each cycle in the total mileage of private cars for the three families of cycles, i.e. the share of total mileage that it represents in Europe. These weights are then used as emission factor weighting coefficients specific to each cycle to calculate an aggregated emission factor specific to each category of vehicle for a family of cycles.

The samples and analyses of non-regulated pollutant cycles (VOC and PAH) were performed

for 4 driving cycles:
- the *Inrets urbain fluide court* cycle repeated 15 times after cold starting, at an average speed of 19.0 km/h, used to characterise cold emissions;
- the same *Inrets urbain fluide court* cycle repeated 15 times after hot starting;
- the *VP faible/forte motorisation urbain* cycle after hot starting, at an average speed of 18.3 km/h (and 19.3 km/h);
- the *VP faible/forte motorisation autoroute* cycle after hot starting, at an average speed of 119.0 km/h (and 121.8 km/h).

Test conditions

All the cycles except one were monitored with hot engines. To bring the temperature of the start of the measurement cycle in line with that at stopping, a warm up period was incorporated by rolling on the test bench at 70 km/h for a quarter of an hour, generally followed by a preconditioning cycle.

A total of 450 tests (vehicle x cycle) were carried out from November 2000 to September 2002. Ambient conditions were on average from 19.7°C, 994 hPa and 44% humidity, with standard deviations of respectively 3.3°C, 5 hPa and 8%. These experimental conditions were therefore relatively variable and corresponded to variations observed in the Lyon region.

Sampling and analysis of regulated pollutants

Exhaust gases were sampled at constant flow using a constant volume sampler (CVS) continuously, with a bag or filter. The regulated pollutants were analysed using classical methods (infrared adsorption for carbon monoxide CO and carbon dioxide CO_2; flame ionisation for total hydrocarbons HC; chemiluminescence for nitrogen oxides NOx; and weighing for particles), or evaluated by calculation (fuel consumption by carbon atom balance).

Sampling and analysis of volatile organic compounds (VOC)

The family of volatile organic compounds groups a vast array of compounds belonging to the following groups, of which we measured: 28 alkanes (saturated), 8 alkanes / alkynes (unsaturated), 5 unsaturated ramified linear C_2 to C_6, 27 monoaromatic hydrocarbons, 3 polyaromatic hydrocarbons, and 13 carbonyl compounds (11 aldehydes and 2 ketones). We also divided these compounds into hydrocarbons of low molecular weight called “light” (C_2 to C_6), and hydrocarbons of high molecular weight called “heavy” (C_6 to $C_{15\ and\ +}$).

Sampling of these VOC was done with two adsorbent cartridges: an active carbon cartridge, Carbotrap B and C, and Carbosieve SIII (active carbon) for hydrocarbons C_2 to C_6, and a Tenax cartridge for hydrocarbons C_6 to $C_{15\ and\ +}$.

Analysis of the samples taken was done by gaseous phase chromatography equipped with a thermal desorption system. The hydrocarbons of low molecular weight were detected by flame ionisation, whereas the “heavier” hydrocarbons were identified by mass spectrometry. Chromatography for the analysis of “light” VOC was done using a gaseous phase chromatograph equipped with a Perkin Elmer Autosystem FID detector coupled with a Turbomatrix TD thermal desorber. The device used to measure the “heavy” VOC was an EM 640 from Bruker, in its normal configuration, namely gaseous phase chromatography (CG) coupled with a mass spectrometer (MS). Identification of compounds was done by mass spectrometry and by comparison with the databases of reference products (NIST library) and confirmation by the dwell time of the standards injected.

Sampling and analysis of aldehydes and cetones

The method used for measuring these carbonyl compounds was developed during previous works [16]. We used a cartridge with a silicon solid phase impregnated with 2,4 DNPH for sampling.

The hydrazones derived from carbonyl compounds obtained after elution of the cartridge in acetonitrile were then separated by liquid chromatography in stationary phase, an Alltima C18 50 column 250 mm long with an internal diameter of 4.6 mm, and using a polar mobile phase composed of three solvents: water (H_2O), acetonitrile (ACN) and tetrahydrofurane (THF). The device used was a Spectra Physics P4000 chromatograph. Detection of the products was done using a UV lamp with a wavelength of 365 nm.

Sampling and analysis of polyaromatic hydrocarbons (PAH)

We analysed the 16 PAH recommended by the US Environment Protection Agency according to their carcinogenic and mutagenic power. See table 3 for the list and their classification by the International Association for Research on Cancer [17-18] according to their toxicity: Acenaphthene Ace, Acenaphtylene Acy, Anthracene An, Benzo[a]anthracene BaA, Benzo[b]fluoranthene BbF, Benzo[k]fluoranthene BkF, Benzo[ghi]perylene BghiP, Benzo[a]pyrene BaP, Chrysene Chr, Dibenzo[ah]anthracene DBahA, Fluoranthene F, Fluorine Flu, Indeno[1,2,3-cd]pyrene IP, Naphtalene N, Phenanthrene Phe, Pyrene P.

16 PAH measured (and their IARC classification)															
Ace	Acy	An	BaA	BaP	BbF	BghiP	BkF	Chr	DBahA	F	Flu	IP	N	P	Phe
-	-	3	2A	2A	2B	3	2B	3	2A	3	3	2B	-	3	3
12 least volatile PAH															
		An	BaA	BaP	BbF	BghiP	BkF	Chr	DBahA	F		IP		P	Phe
6 most carcinogenic PAH															
			BaA	BaP	BbF		BkF		DBahA			IP			

Table 3: List of 16 PAH measured, the 12 least volatile PAH and the 6 most carcinogenic PAH, according to the IARC classification for humans (group 1: carcinogenic, group 2A: probably carcinogenic, group 2B: possibly carcinogenic, group 3: not classifiable as to its carcinogenicity, group 4: probable non- carcinogenic).

The PAH were sampled at the end of the CVS dilution tunnel using two successive cartridges. The packing, Teflon wool and Amberlite XAD2 resin were purified in the laboratory by two successive Soxhlet cycles of 8 hours with cyclohexane. The two sampling media were subjected to special treatment before the analysis as such, i.e. extraction of PAH from the media by an organic solvent, concentration of the extract and purification of the matrix obtained. After evaporation under nitrogen flow until the eluate was almost dry, the purified sample was retreated with 0.5 ml acetonitrile.

The study was carried out on a Merck-Hitachi chromatograph equipped with a LiChroCart column, fed by an injection loop with a volume fixed at 20 µl and coupled with adsorption and fluorescence spectrometers. Elution was performed using ACN/H_2O in mobile phase at a flow of 1 ml/mn.

Result presentation method

All the emission and consumption results, integrated in one cycle, are represented by unit of weight per unit of distance travelled (g/km). CO, CO_2, consumption and particles are expressed in real weight emitted, whereas HC and NOx are expressed in equivalent weights of CH_4 and NO_2 respectively.

In addition, when the objective was to evaluate the influence of a parameter without taking kinematics conditions into account, for example, the influence of emission standard, we calculated unit emissions called aggregated. They were built by weighting the unit emissions of the same family of cycles with the weight of each cycle in the traffic under study, i.e. by the share of the mileage it represents (see Table 2). It was thus possible to calculate an urban emission according to *VP faible motorisation* cycles on the basis of the emissions measured as a function of *VP faible urbain dense* cycles and *VP faible motorisation urbain fluide* cycles weighted by the weights of these two 2 traffic situations in urban use.

2. RESULTS

Below we examine the influence on driving cycle emissions and then on the category of vehicle. The influence of cold starting on emissions is treated in a specific report [19], although certain aspects related to non-regulated pollutants are dealt with below.

Regulated pollutants

Since the regulated pollutant emissions were measured for all driving conditions (urban, rural, highway) by using the three families of cycle (*Artemis*, *VP faible/forte motorisation* over 3 cycles, and *VP faible/forte motorisation* over 4 cycles), it was possible to appreciate the global influence of the family of cycles on the emissions, based on the aggregated emissions, and thus appreciate the advantage of simplifying the procedures by having a single set of cycles rather than cycles appropriate for each category of vehicle. The results, for which Fig. 2 illustrates an example for Euro 2 vehicles, shows considerable variations according to type of pollutant and vehicle. The emission ratios as a function of *VP faible/forte motorisation* on emissions according to *Artemis* were:

- for CO, from 42 to 113% for gasoline vehicles, and from 92 to 175% for diesel vehicles,
- for HC, from 85 to 155% with little difference between the two fuels,
- for NOx, from 87 to 120% with little difference between the two fuels,
- for particles, from 40 to 142% for diesel,
- for CO_2 and consumption, from 98 and 102% for diesel, and close to 98% for gasoline vehicles.

Apart from the carbon dioxide emissions of gasoline vehicles systematically over-estimated by *Artemis*, it is difficult to draw simple conclusions from these results. Nonetheless it appears that the driving cycle quality can have a relatively strong impact on emissions. It should be noted that the three families of cycle are all representative of real driving conditions, and therefore far removed from regulated cycles. More thorough analysis of the impact of kinematics and the kinematics parameters of cycles is presented elsewhere [20].

The calculation and curve of aggregated emissions as a function of vehicle category (fuel, emission standard), for which an example is presented in Fig. 3 for NOx, permits evaluating the influence of the standard and comparing gasoline and diesel powers of equivalent standards.

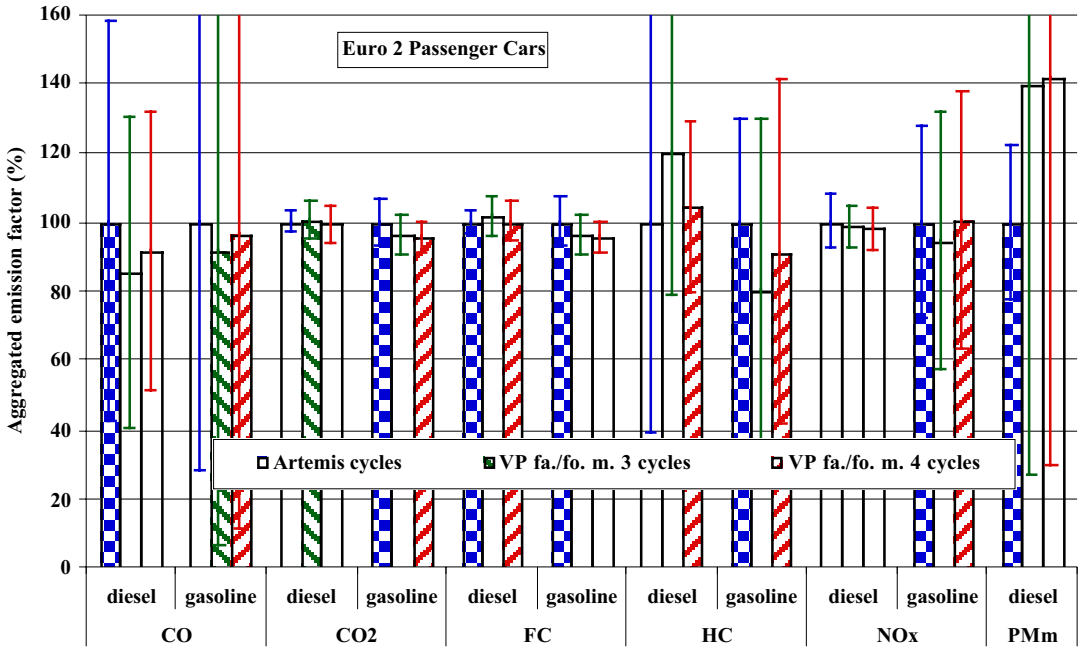

Figure 2: Influence of cycle family (Artemis, VP faible/forte motorisation in 3 cycles, 4 cycles) on the different aggregated emission factors of Euro 2 vehicles (Artemis = 100).

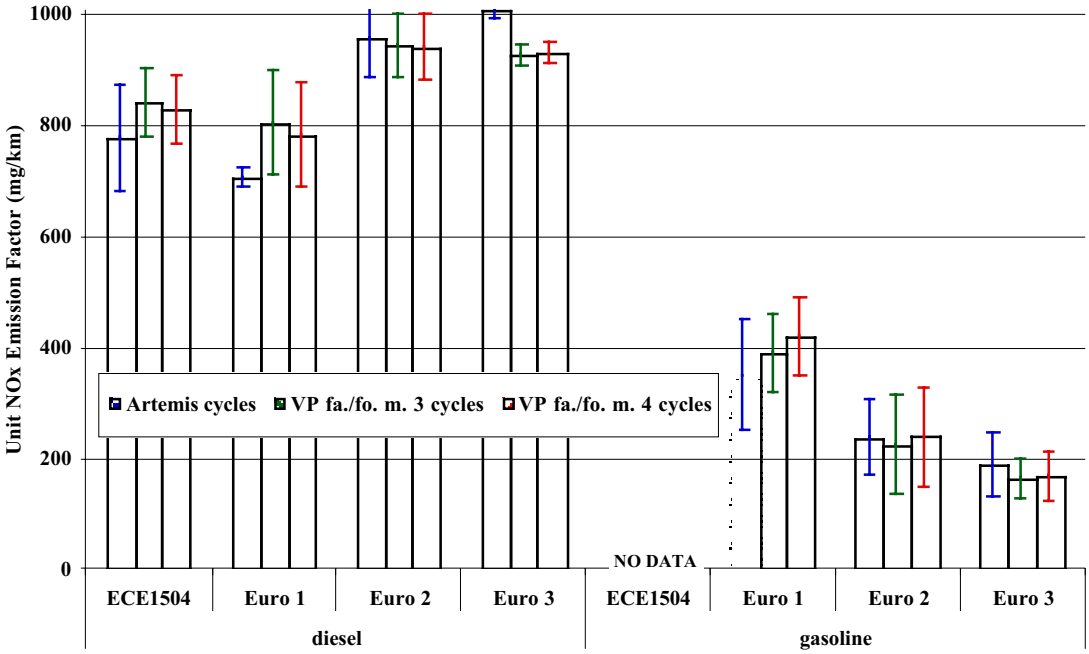

Figure 3: Progression of NOx emission factor with regulation.

Changes made to the standard have had a very positive impact on gasoline CO, HC, NOx, emissions and diesel particles: from Euro 1 to Euro 3, CO emissions have been reduced by a factor of 4 for gasoline, and by 12 for diesel. These figures are respectively 7 and 2 for HC; gasoline NOx emissions and diesel particles have been divided by a factor of 2. CO_2 emissions and consumption have changed relatively little; thus it is difficult to make conclusions given the small samples and changes in vehicle weights and powers that have

occurred in parallel with the progression of emission standards. The black point remains the diesel NOx emissions, which, after a slight fall from ECE 1504 to Euro 1, increased by nearly 16% from Euro 1 to Euro 3. Although these figures should be treated with caution, the situation does not appear to have improved.

The comparison of two gasoline and diesel powers is sufficiently solid for Euro 2 vehicles, whose samples were composed of 10 and 6 vehicles respectively. In this case, the gasoline vehicles emitted 5 times more CO than the diesel ones, 70% more HC, 1 to 2% more CO_2 and consumption. However, diesel vehicles emitted 4 times more NOx than the gasoline vehicles. There is even a tendency towards an increase of CO, NOx, and CO_2 emissions and consumption when Euro 3 vehicles are taken into account.

VOC and carbonyl compounds

The distribution of VOCs and carbonyl compounds is evaluated on the basis of hot aggregated emissions (see Table 4) as a function of *VP faible/forte motorisation* cycle.

VP faible/forte motorisation cycle		gasoline			diesel			
		Euro 1	Euro 2	Euro 3	1504	Euro 1	Euro 2	Euro 3
alkanes	(%)	5.4	12.4	6.8	17.9	27.5	14.4	17.6
alkenes + alkyne	(%)	0.6	1.3	2.6	4.3	17.7	5.5	1.3
aldehydes	(%)	0.2	0.5	0.2	3.4	7.8	1.5	0.4
ramified C2-C6	(%)	0.4	2.7	2.2	6.4	8.2	5.7	11.5
ketones	(%)	0.4	0.2	0.1	0.4	0.8	0.6	0.2
polyaromatics	(%)	0.0	0.0	0.0	0.0	0.2	0.8	0.0
monoaromatics	(%)	93.0	82.9	88.1	67.7	37.7	71.5	69.0
total VOC	(%)	100	100	100	100	100	100	100
	(mg/km)	3451	845	1044	642	233	793	820

Table 4: Distribution of aggregated VOC emissions by molecular family in %, and the total of VOC emissions in mg/km, as a function of fuel and regulations.

Inrets urbain fluide court cycle		gasoline			diesel			
		Euro 1	Euro 2	Euro 3	1504	Euro 1	Euro 2	Euro 3
alkanes	(%)	4.6	6.5	1.7	5.6	88.2	0.7	-7.1
alkenes + alkyne	(%)	0.4	1.9	0.0	2.7	0.9	6.5	0.9
aldehydes	(%)	-0.1	0.1	0.0	0.7	4.0	0.1	0.5
ramified C2-C6	(%)	0.0	0.0	0.1	0.0	-30.2	1.8	-16.9
ketones	(%)	0.0	0.0	0.0	0.3	1.2	0.0	0.3
polyaromatics	(%)	0.0	0.0	0.0	0.0	0.2	0.2	0.0
monoaromatics	(%)	95.0	91.5	98.3	90.9	35.7	90.6	122.2
total VOC	(%)	100	100	100	100	100	100	100
	(g)	52.3	100.3	91.0	9.4	1.7	5.8	5.8

Table 5: Distribution of excess cold start emissions of VOC by molecular family in %, and total of excess emissions of VOC in g, as a function of fuel and regulations.

Whatever the vehicle category, the best represented families are saturated hydrocarbons (5 to 28% of the total in mass as a function of vehicle) and above all aromatic hydrocarbons (from 38 to 93%). The share of monoaromatics is highest for gasoline vehicles (close to 88%), whereas it is close to 62% for diesel vehicles. The share of alkanes is higher on average for diesel (19%) than for gasoline (8%) vehicles. On average, the shares of alkenes, aldehydes

and ramified C_2-C_6 is from 5 to 10 times higher for diesel than for gasoline vehicles.

The influence of the emission standard on these distributions is fairly low, less than the influence of the fuel.

We then calculated the distribution of VOC and carbonyl compounds by family for over-emission on cold starting, in comparison with absolute emissions in terms of weight as a function of the hot and cold *Inrets urbain fluide court* cycle (see Table 5). The distributions are quite close to the hot distributions, with an even greater share for the monoaromatics and the disappearance of aldehydes, ramified C_2-C_6 and ketones for gasoline vehicles alone.

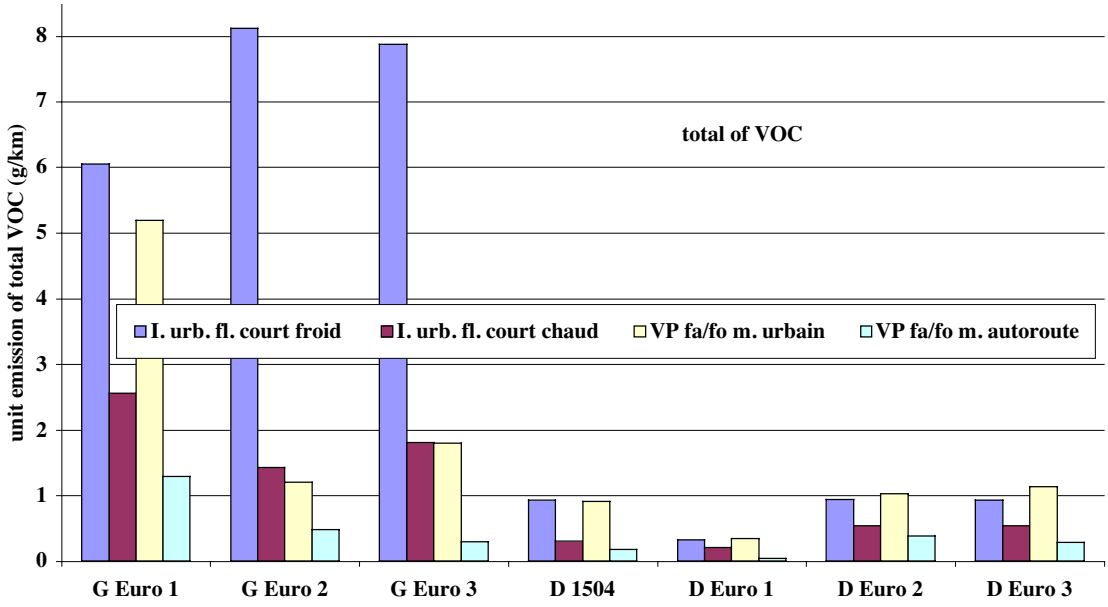

Figure 4: Average emissions of VOC in g/km, as a function of test cycle, fuel and regulations.

The impact of successive standards on VOC emitted hot is very positive for gasoline vehicles and rather negative for diesel vehicles, as shown by the aggregated hot emission factors on the bottom line of table 4. These changes can be seen hot whatever the cycle (see Fig. 4). On the contrary, cold, the change is quite negative for gasoline vehicles, and quite low and even negative for diesel vehicles. Regarding gasoline vehicles, which emit more VOC than diesel ones, their cold emissions increase and hot emissions decrease, whereas the emissions of diesel vehicles decrease from standard ECE 1504 to Euro 1, then increase again from Euro 1 to Euro 2 and 3.

Cold start VOC emissions are considerably higher than hot start emissions, by a factor of nearly 4 for gasoline vehicles and a factor close to 2 for diesel vehicles. These high factors are first due to the weight of the monoaromatics in the total VOC. However, excess cold-start emission can be substantially lower for certain families of VOC and powers. This is so with alkanes, aldehydes, ramified C_2-C_6 and ketones in most cases; there are even under-emissions in several cases, in particular for the ramified C_2-C_6 of Euro 1 and 3 diesel vehicles, and the ketones of Euro 2 and 3 gasoline vehicles.

We then performed the same calculations by molecular family. The aggregated hot start emissions changed as follows with successive standards:

- clear decrease for alkanes, aldehydes, ketones and monoaromatics of gasoline vehicles, as well as for the aldehydes of gasoline vehicles,

- little change for alkenes and polyaromatics whatever the fuel, or for the ketones and monoaromatics of diesel vehicles,
- clear increase for ramified C_2-C_6 whatever the fuel, and for the alkanes of diesel vehicles.

The differences between gasoline and diesel vehicles are considerable in several cases: diesel vehicles emit far more aldehydes, ramified C_2-C_6 and polyaromatics, though substantially fewer monoaromatics.

What is more, figure 4 shows the influence of different hot start cycles on the total VOC emitted. Whatever the type of vehicle, emissions on the highway are far lower than under urban conditions; the ratio varies from 2.5 to 7.8. Furthermore, it should be noted that the two hot start *Inrets urbain fluide court* cycle and the *VP faible/forte motorisation urbain* cycle, whose average speeds are very similar, do not always give similar emissions. Although this is the case for Euro 2 and 3 gasoline vehicles, the *Inrets* cycle gives emissions 2 times lower than the *VP* cycle for the Euro 2 and 3 diesel vehicles. The differences between urban and highway conditions by molecular family are similar to what was observed for total VOC.

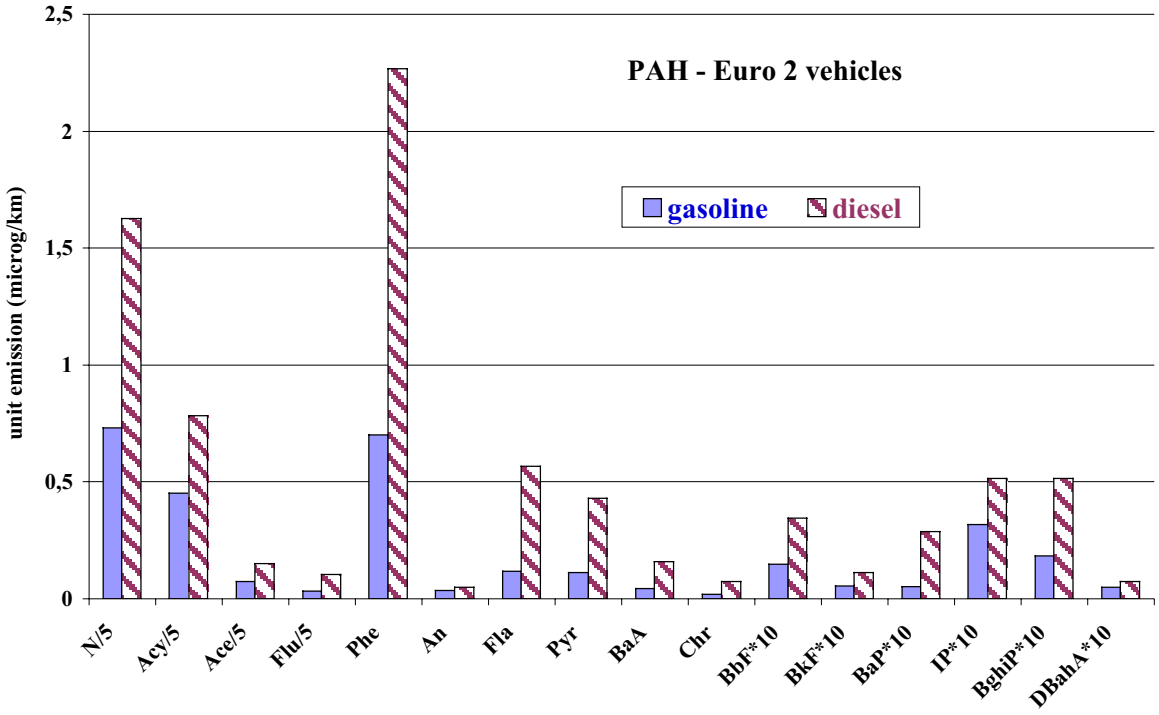

Figure 5: Average distribution of PAH for Euro 2 vehicles (gasoline and diesel) within aggregated hot start emission.

Polycyclic aromatic hydrocarbons (PAH)

Figure 5 shows an example of the distribution of the 16 PAH measured for Euro 2 gasoline and diesel vehicles. It can be seen that Acy is rarely detected and quantified. There appears to be a correlation between the emission values and the volatility of the different PAH: N at 2 cycles predominates (~50-90 % of the total of the 16 PAH expressed in mass for gasoline vehicles, ~20-50 % for diesel vehicles). A clear decrease can then be seen for the PAH at 3 cycles (Ace, Flu, An, Phe), 4 cycles (Fla, Pyr, BaA, Chr) then 5 and 6 cycles (BbF, BkF, BaP, BghiP, IP, DbahA) with respectively 25, 5 and 1% of the total mass. This distribution was also observed for the results obtained by Mi et al. [21]. The distributions obtained for all the vehicles and for each cycle were very similar to those in Fig. 5.

The yields are very low (5 to 40%) while the analytical errors are considerable for the highly volatile PAH (N, Ace, Acy and Flu), leading to substantial losses during the extraction and purification procedures. Furthermore, all the results are presented with the total of the 12 least volatile PAH and the total of the 6 PAH recognised as being the most carcinogenic (see Table 2).

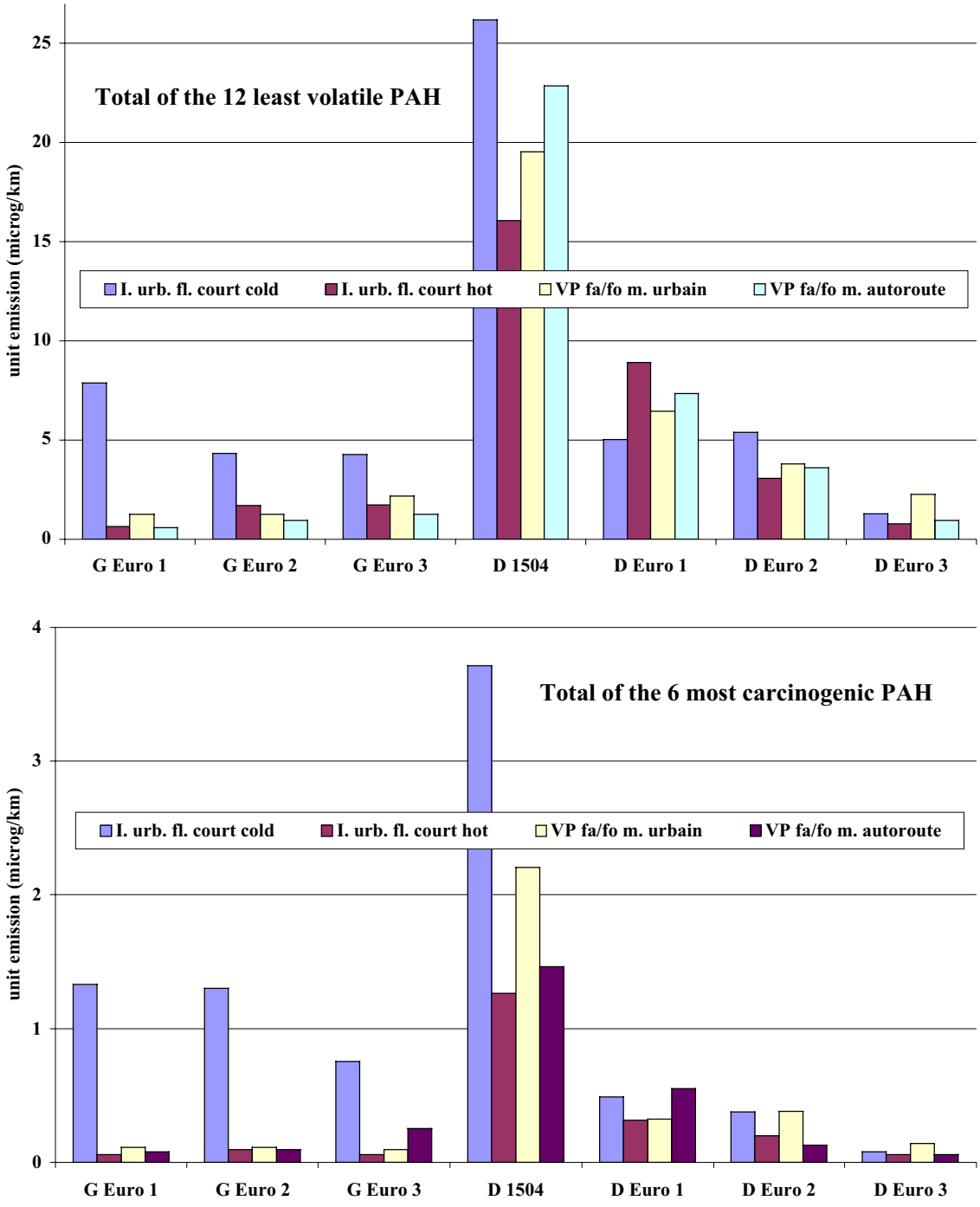

Figure 6: Average emissions of the total of 12 least volatile PAH on the one hand, and the total of the 6 most carcinogenic PAH on the other, as a function of fuel, regulations and driving cycle.

The averages of the totals of the 12 and 6 PAH for gasoline and diesel vehicles are represented for the 4 cycles in Fig. 6. The values for the vehicles corresponding to Euro 1

gasoline regulations and diesel ECE 1504, Euro 1 and Euro 3 only concern a very limited number of vehicles and require confirmation.

Cold starting had little influence on diesel vehicle emissions, whether the 12 or 6 PAH were taken into consideration. Regarding gasoline vehicles, the emissions were clearly higher for cold starting than for hot starting, with a factor varying from more than 10 to 2 for the total of the least volatile PAH, and a factor of nearly 20 when considering only the 6 most carcinogenic PAH. This trend confirms the results obtained previously [22-24]. The influence of driving conditions with hot starting (urban and highway) is not inconsiderable though varies somewhat as a function of fuel and regulations.

Globally, regulations have a definitely positive influence on diesel vehicle emissions, though this influence is debatable for gasoline vehicles. In order to make a more global evaluation of the influence of fuel and regulations, we calculated the aggregated hot start emissions in the same way as for the other pollutants. They are the synthesis of emissions measured as a function of *VP faible/forte motorisation urbain* and *VP faible/forte motorisation autoroute*. The results, shown in Fig. 7, confirm the very positive impact of regulating diesel vehicles, since the emission of the 12 least volatile PAH has been divided by a factor of 3 from standard ECE 1504 to standard Euro 1, then by a factor of 5 from Euro 1 to Euro 3. These factors are even higher for the 6 most carcinogenic PAH (respectively 5 and 5).

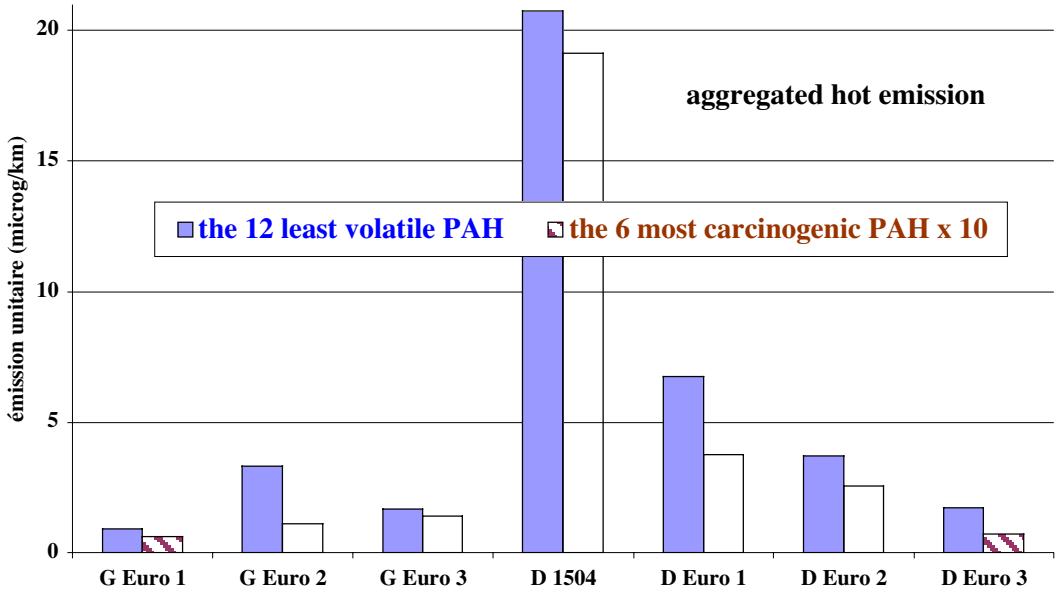

Figure 7: Aggregated average hot start emissions (microg/km) of the total of the 12 least volatile PAH on the one hand, and the total of the 6 most carcinogenic PAH on the other (x 10).

As for gasoline vehicles, progression related to regulations of the total of the 12 PAH was rather negative, with an increase in the region of 15% from Euro 1 to Euro 2, then nearly 55% from Euro 2 to Euro 3.

The difference between gasoline and diesel vehicles was very marked for vehicles up to Euro 2. It was practically nil for Euro 3 regulation regarding the 12 PAH; for the 6 carcinogenic PAH considered alone, the Euro 3 diesel vehicles emit half as much carcinogenic PAH as gasoline vehicles.

On average, for each of the two fuels and for hot start cycles, the distribution of PAH between

gaseous and particulate phases is shown in Fig. 8, and synthesised in Table 8 for Euro 2 vehicles.

The distribution of PAH between gaseous and particulate phases depends on their volatility. The most volatile PAH (N, Acy, Ace, Flu) are mostly in gaseous phase whereas the other PAH are mostly adsorbed on the particles. Two thirds of the carcinogenic PAH are adsorbed on the particles, whatever the fuel.

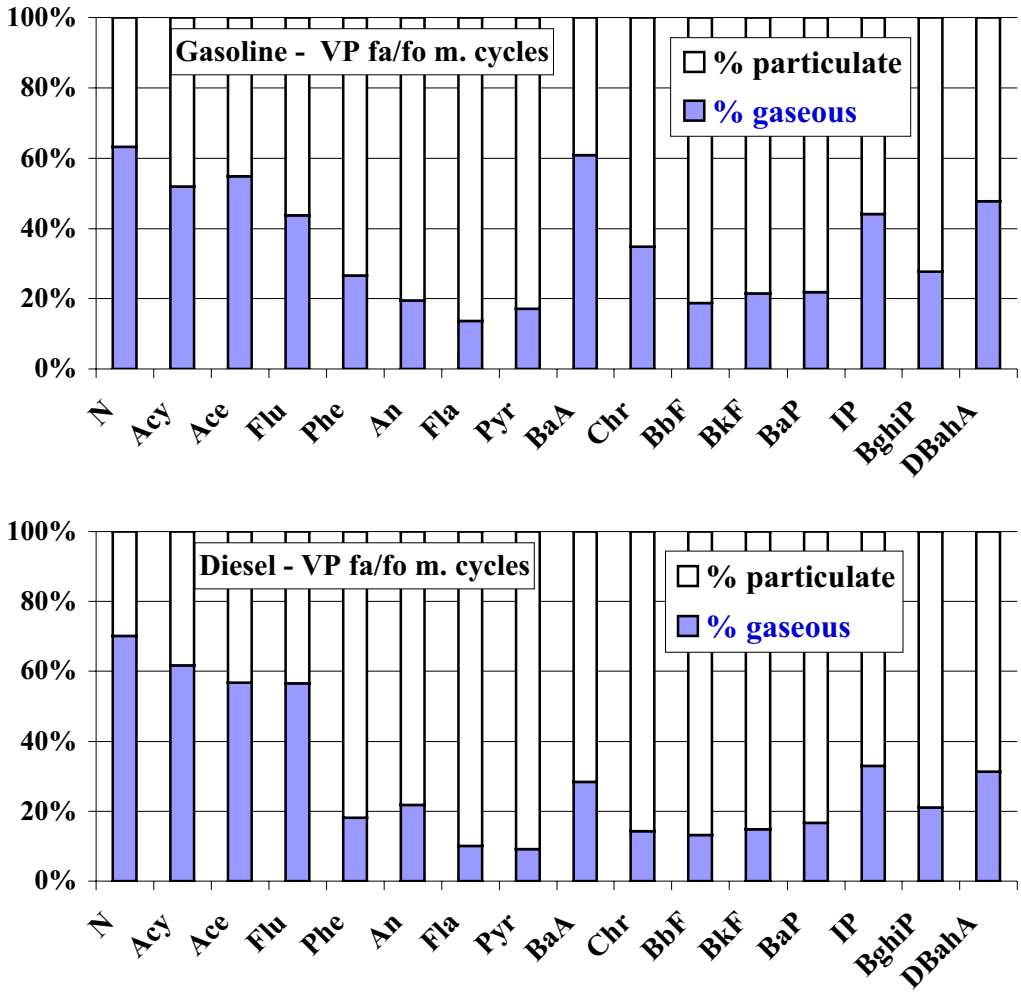

Figure 8: Mean distributions between gaseous and particulate phases of aggregated hot start emissions of 12 PAH, by fuel.

Totals of PAH	Gasoline	Diesel
4 volatile PAH (N, Acy, Ace, Flu)	53 / 47	61 / 39
12 PAH (less volatile)	30 / 70	20 / 80
6 PAH (carcinogenic)	35 / 65	23 / 77

Table 8: Mean distribution between gaseous/particulate phases of aggregate hot start Euro 2 vehicle emissions, in %..

The quantity of PAH adsorbed on the particles is much higher for diesel vehicles than for gasoline ones.

Consequently, it is vital to carry out sampling of PAH in both gaseous and particulate phases to obtain good quantification of these pollutants in vehicle emissions, and more especially for very volatile compounds (PAH from two to four cycles).

3. CONCLUSION

Emissions of regulated pollutants were measured over a large number of representative driving cycles, in particular according to the European *Artemis* cycles and the *VP faible/forte motorisation* cycles adapted to the vehicle, which were the families of cycle formulated for this occasion. The results show that the family of cycles, i.e. the way it is structured and its kinematic properties, has a non-negligible impact on global emissions, all driving conditions confounded. However, the influence of the specific conditions of each cycle is greater, as has been shown many times previously.

Since the measurement campaign concerned seven categories of private car (gasoline and diesel with different emissions standards), it is possible to evaluate the impact of changes in emission standards and compare gasoline and diesel powers. The decrease of unit emissions from the Euro 1 to Euro 3 standards is almost systematic and considerable; the reduction factors vary from two to twelve according to case. The only negative point on the table is the significant increase of NOx emissions from diesel vehicles and near stability of unit CO_2 emissions.

Diesel vehicles always appear less pollutant than gasoline vehicles for CO, HC and CO_2, with the variation tending to increase standard by standard. By contrast, diesel vehicles emit nearly four times more NOx than gasoline vehicles, with this variation increasing markedly, and they obviously emit more particles, though these emissions have decreased in absolute value (excluding particle filters, not tested here).

The variations between the fuels observed for the total hydrocarbon HC emissions can be seen for VOC though not for PAH. Although diesel vehicles emitted approximately twice as much PAH as gasoline vehicles, recent technologies have considerably reduced this difference. The impact of increasingly severe standards on HC emissions was very positive; it remains so for gasoline and diesel PAH emissions and gasoline VOC (although less clearly), though is rather negative for diesel VOC. The PAH results agree with those obtained during previous studies regarding the trends observed for both vehicle technologies.

The distribution of VOC by molecular family highlights the essential role played by monoaromatics, nearly 88% for gasoline vehicles and 62% for diesel. The second family in terms of weight per family is composed of the alkanes which make up respectively 8 and 19% of total VOC measured for gasoline and diesel vehicles.

Most of the volatile PAH were observed in the gaseous phase, whereas the less volatile and carcinogenic PAH were adsorbed more in particulate phase.

These conclusions must however be seen in relative terms given the small vehicle samples, excepting the Euro 2 standard. Confirmation is required from the analysis of measurements by the other partners of the Artemis project who have conducted similar campaigns.

These results permit extending knowledge of emission factors to the most recent passenger cars on the one hand, and obtaining the emission factors of a very large number of volatile organic compounds and polyaromatic hydrocarbons, under totally realistic conditions, on the other. Thus it is the indispensable basis for an emissions inventory for the period 1995-2010, in which Euro 2 and 3 vehicles form the majority.

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